

Long-Term Wet and Dry Deposition of Total and Methyl Mercury in the Remote Boreal Ecoregion of Canada

JENNIFER A. GRAYDON,^{*,‡}
VINCENT L. ST. LOUIS,[‡]
HOLGER HINTELMANN,[§]
STEVE E. LINDBERG,^{||}
KEN A. SANDILANDS,[⊥]
JOHN W. M. RUDD,[#] CAROL A. KELLY,[#]
BRITT D. HALL,[∇] AND
LINNEA D. MOWAT[#]

Department of Biological Sciences, University of Alberta,
Edmonton, Alberta, Canada, T6G 2E9, Department of
Chemistry, Trent University, 1600 West Bank Drive,
Peterborough, Ontario, Canada, K9J 7B8, Oak Ridge National
Laboratory, P.O. Box 2008, Oak Ridge, Tennessee, 37831-6083,
Freshwater Institute, Fisheries and Oceans Canada, 501
University Cres., Winnipeg, Manitoba, Canada, R3T 2N6, R&K
Research, Inc., 675 Mt. Belcher Heights, Salt Spring Island,
British Columbia, Canada V8K 2J3, and Department of
Biology, University of Regina, 3737 Wascana Parkway, Regina,
Saskatchewan, Canada, S4S 0A2

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Although a positive relationship between atmospheric loadings of inorganic mercury (Hg(II)) to watersheds and concentrations of methyl mercury (MeHg) in fish has now been established, net wet and dry deposition of Hg(II) and MeHg to watersheds remains challenging to quantify. In this study, concentrations and loadings of total mercury (THg; all forms of Hg in a sample) and MeHg in open area wet deposition, throughfall, and litterfall were quantified at the remote Experimental Lakes Area in the boreal ecoregion, NW Ontario, Canada. Between 1992 and 2006, mean annual THg and MeHg loadings in the open were 36 ± 17 and 0.5 ± 0.2 mg ha⁻¹, respectively. Throughfall THg and MeHg loadings were generally 2–4 times and 0.8–2 times higher, respectively, than loadings in the open. Loadings of both THg and MeHg were highest under an old growth spruce/fir canopy and lowest under a deciduous maple canopy, whereas loadings under young jack pine and wetland spruce/pine/alder canopies were intermediate. Litterfall generally represented the largest input of THg (86–105 mg ha⁻¹) and MeHg (0.7–0.8 mg ha⁻¹) to the landscape on an annual basis. Using the “direct” method of estimating dry deposition (throughfall + litterfall – open loadings), we calculated that annual dry deposition of THg and MeHg under forest canopies ranged from 105 to 201 mg ha⁻¹, whereas dry deposition of MeHg ranged from 0.7 to 1.2 mg ha⁻¹. Photoreduction and

emission of wet-deposited Hg(II) from canopy foliage were accounted for, resulting in 3–5% (5–6 mg ha⁻¹) higher annual estimates of dry deposition than via the direct method alone. Net THg and MeHg loadings to this remote landscape were lower than at any other previously studied forested site globally. This study shows that THg and MeHg loading can be extremely variable within a heterogeneous boreal landscape and that processes such as Hg photoreduction and emission from foliage should be considered when estimating dry deposition of Hg.

Introduction

The positive relationship between atmospheric loadings of inorganic mercury (Hg(II)) to watersheds and concentrations of methyl mercury (MeHg) in fish has now been well-established 1. For example, the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) recently showed that an experimental increase in Hg(II) loading to a lake and its catchment (at rates relevant to atmospheric deposition) resulted in an increase in MeHg production and concentrations in aquatic biota within months 2. This is because following deposition, Hg(II) can be converted to MeHg in anaerobic environments such as lake sediments 3, hypolimnetic waters 4, and wetlands 5. MeHg is biomagnified through aquatic food webs and can reach concentrations in fish that are high enough to pose health risks to vertebrate consumers.

Human activities such as coal burning have greatly enhanced emissions of gaseous elemental Hg(0) to the atmosphere, as well as emissions of oxidized reactive gaseous Hg(II) (RGM) and Hg(II) bound to particulates (HgP) 6. Whereas the predominant form of Hg in the atmosphere is Hg(0) (>95%), Hg is deposited to landscapes in precipitation primarily as Hg(II) because of its high solubility in rain 6. In addition to wet deposition of Hg in precipitation, there can also be dry deposition of Hg(0), HgP, and RGM to watersheds. Because of the large surface area of receptor sites on foliage, dry deposition of Hg is typically much more significant in forested areas than in the open. Hg(0) is primarily absorbed through foliar stomata and deposited to forest soils in litterfall while RGM and HgP adsorb directly to foliar surfaces and can be washed to the forest floor when precipitation penetrates the forest canopy as throughfall 7. RGM has a higher deposition velocity (V_d) than Hg(0) and is consequently dry-deposited at a faster rate than Hg(0). However, larger concentrations of Hg(0) in the atmosphere offset its lower V_d , making it likely that the dry deposition flux of Hg(0) via stomatal uptake is a large component of total dry deposition.

Dry Hg deposition rates have been estimated using three primary approaches: (1) the “direct” method, which involves subtracting wet deposition in open areas from the sum of loadings in throughfall and litterfall, (2) “inferential” methods that use concentrations of atmospheric Hg species and meteorological measurements to model dry deposition, and (3) micrometeorological methods including gradient and modified Bowen ratio techniques 6. However, all these approaches are considered experimental and there remain large uncertainties associated with estimating dry Hg deposition. For example, photoreduction and emission to the atmosphere of newly wet-deposited Hg from foliage is poorly understood, but failure to account for this emission can result in an underestimate of the dry Hg flux. Watershed to global scale Hg mass balance models require accurate estimates of dry Hg deposition, and further study is required to elucidate the factors complicating its measurement.

* Corresponding author phone: (780) 492-0900; fax: (780) 492-9234; e-mail: jgraydon@ualberta.ca.

[‡] University of Alberta.

[§] Trent University.

^{||} Oak Ridge National Laboratory; now Graeagle, CA.

[⊥] Fisheries and Oceans Canada.

[#] R&K Research, Inc.

[∇] University of Regina.

We have been examining the biogeochemical cycling of Hg at the remote Experimental Lakes Area (ELA) field station in the boreal ecoregion of NW Ontario since the early 1990s. The ELA is world-renowned for whole-ecosystem experimentation, and of relevance to this study is our historic involvement in experiments examining environmental impacts of hydroelectric reservoir creation and Hg emissions. These experiments required detailed measurements of net Hg loadings to the region, and as a result, we have been quantifying wet deposition of total Hg (THg; all forms of Hg in a sample) and MeHg in the open at the ELA since 1992. We have also been estimating dry deposition of THg and MeHg to canopy foliage at the ELA since 1998 using the direct method described above. In this study, we present (1) long-term concentrations and net loadings of THg and MeHg in open area precipitation (1992–2006) and in throughfall and litterfall under four different forest types (2001–2006) and (2) new estimates of THg and MeHg dry deposition based on the difference between loadings in the open and in throughfall plus litterfall.

Materials and Methods

Site Description. From 1992–2000, open precipitation was collected at the ELA meteorological site located ~0.5 km west of the ELA base station on Lake 239 (Figure S1 in the Supporting Information). This site is situated on a bedrock knoll surrounded by a jack pine (*Pinus banksiana*)/white birch (*Betula papyrifera*) forest regenerated following a fire in 1980.

From 2001–2006, open precipitation, throughfall, and litterfall were collected in the upland and wetland portions of the Lake 658 watershed as part of METAALICUS. Lake 658 is 8 ha in surface area and is surrounded by a 43-ha watershed. A 6-ha section in the northwest portion of the watershed was logged in 1978 and now supports a deciduous forest of red maple (*Acer rubrum*) and white birch. In 1983, a fire burned most of the south side of the watershed and a portion of the north shore. This 21-ha burned area now contains a dense canopy of young jack pine. The portion of the upland that was not burned or logged (14 ha) is dominated by mature black spruce (*Picea mariana*) and balsam fir (*Abies balsamea*). A 2-ha wetland connected to the western portion of the lake is composed of black spruce, jack pine, and alder shrubs (*Alnus* sp.).

Concentrations of THg and MeHg in Open Area Precipitation, Throughfall, and Litterfall. Precipitation and throughfall sampling occurred primarily during the ice-free season (May through October). At the ELA meteorological site, wet deposition samples were collected on a per event basis between 1992–1993 and 1998–2000. Just before precipitation events, clean 250-mL wide-mouth Teflon containers were deployed on acid-washed plexiglass trays elevated on wooden posts. Immediately following deposition events, samples were transferred into clean 125–250-mL Teflon bottles. THg samples were preserved with concentrated trace-metal grade (TMG) HCl equal to 0.2% of sample volume, whereas MeHg samples were frozen until analysis. From 2001 to 2006, composite open area wet deposition samples were collected using an automated wet deposition collector (Aerochem Metrics, Figure S2 in the Supporting Information) installed on a peninsula in the METAALICUS watershed (Figure S3 in the Supporting Information). One acid-washed glass funnel (7.3 cm diameter) was attached via a piece of Teflon tube and Teflon compression fitting to a closed 2-L Teflon jar containing 1 mL of TMG HCl. An acid-washed, circular Teflon grid placed at the base of the funnel was used to filter coarse debris. MeHg and THg samples were collected following ~20–30 mm of deposition and further preserved using TMG HCl equal to 0.2% of sample volume. A second glass funnel (4.5 cm diameter) attached

to a 500-mL polyethylene bottle was used to collect precipitation for SO_4^{2-} analysis. Because industrial processes (especially coal burning) represent large sources of both Hg and SO_4^{2-} to the atmosphere, we used SO_4^{2-} deposition as a proxy to investigate potential industrial sources contributing to Hg deposition at the ELA.

It has been shown that rapid photoreduction of Hg(II) and MeHg in winter snowpacks leads to emission of Hg(0). The net result of this photoreduction is that only Hg remaining in snowpacks at snowmelt enters watersheds to contribute to Hg(II) methylation and bioaccumulation. Therefore, integrated snowpack samples were only collected for Hg analyses at the time of maximum snowpack depth (mid-February to mid-March) to estimate net winter THg and MeHg loadings. Samples were collected from the surface of either Lake 239 (1992–1993 and 1998–1999) or from Lake 658 (2004–2006) using a Teflon core tube (3.5 cm diameter) and then transferred into a clean 2-L Teflon jar. Snow samples were either stored frozen until analyses or melted in a Hg clean laboratory, transferred to clean Teflon bottles, and preserved using TMG HCl as above.

We began collecting throughfall in 2001 using automated collectors deployed under the wetland black spruce/alder canopy, the upland old growth balsam fir/black spruce canopy, and the upland fire-regenerated jack pine canopy (Figure S2 in the Supporting Information) in the METAALICUS watershed (Figure S3 in the Supporting Information). In 2005, additional throughfall collectors were installed in the uplands under the deciduous red maple/birch canopy, as well as under the old growth balsam fir/black spruce and the fire-regenerated jack pine canopies to replicate two of our sites first deployed in 2001 (Figure S3 in the Supporting Information). Samples were collected as described above for the collector in the open. Between 2001 and 2006, integrated snowpack samples for Hg analyses were also collected below forest canopies, close to automated throughfall collectors, as described above for open areas.

Two litterfall collectors were deployed near each automated throughfall collector site between 2001 and 2006. Collectors (625 cm²) were constructed using untreated lumber. A piece of mesh screening was laminated between upper and lower portions of the frame so that samples remained dry and elevated above the ground surface. Samples were collected every year in late October after the majority of deciduous leaves had fallen and once again in early May to collect any litterfall that occurred over winter. Litter remained in the collectors for only a short time before collection as (1) there is minimal mass flux of litter before senescence of shrubs and deciduous tree leaves in the autumn and (2) conifer needles and small tree branches that broke under the weight of snow, fell directly onto the snowpack during winter where they remained frozen until they were deposited into collectors during spring melt. Samples were collected into Ziploc bags. Fall and spring litterfall samples from individual collectors were weighed and then pooled into annual composite samples for THg and MeHg analyses. Samples were stored frozen until they were freeze-dried and homogenized using stainless steel coffee grinders rinsed with deionized water and cleaned with paper towels between samples.

Standard THg, MeHg, and SO_4^{2-} analytical protocols are detailed in the Supporting Information.

Annual THg and MeHg Loadings in Open Area Precipitation, Throughfall, and Litterfall. For all years, areal water volume of snow deposited in the open was obtained using a Nipher snow gauge at the ELA meteorological site. In 2004–2006, under-canopy snowpack water equivalent (SWE) data were obtained from surveys of the throughfall sites in the METAALICUS watershed at the time of snow sampling. Near each automated collector, average areal water volume

TABLE 1. Measured and Volume-Weighted Average Annual Concentrations of THg and MeHg (\pm SD) in Open Area Precipitation and in Throughfall under Four Forest Canopy Types at the ELA

site	annual deposition (mm)	average annual THg concentration (ng L ⁻¹)			average annual MeHg concentration (ng L ⁻¹)			% MeHg
		measured	volume weighted	<i>n</i>	measured	volume weighted	<i>n</i>	
1992–2006 overall open	720 \pm 122	6.1 \pm 2.6	5.7 \pm 3.2	84	0.08 \pm 0.04	0.08 \pm 0.05	79	1.8 \pm 2.2
2001–2006 open ^a	657 \pm 104	5.9 \pm 3.0	5.5 \pm 3.2	51	0.08 \pm 0.05	0.07 \pm 0.05	49	2.0 \pm 2.5
wetland	548 \pm 111	19.1 \pm 5.7	17.2 \pm 5.0	50	0.15 \pm 0.06	0.12 \pm 0.05	46	0.9 \pm 1.5
jack pine 1	384 \pm 80	10.0 \pm 0.6	9.5 \pm 1.2	50	0.16 \pm 0.09	0.14 \pm 0.08	40	1.1 \pm 1.0
old growth 1	382 \pm 106	40.8 \pm 6.6	32.8 \pm 6.3	51	0.26 \pm 0.12	0.21 \pm 0.09	36	0.7 \pm 0.6
2005–2006 open ^a	606 \pm 59	7.4 \pm 2.4	7.1 \pm 2.3	19	0.07 \pm 0.06	0.07 \pm 0.05	19	1.1 \pm 0.9
jack pine 2	444 \pm 32	15.4 \pm 3.9	15.2 \pm 3.4	16	0.17 \pm 0.12	0.14 \pm 0.10	13	1.1 \pm 0.8
old growth 2	512 \pm 94	54.9 \pm 0.8	50.4 \pm 0.7	16	0.36 \pm 0.29	0.31 \pm 0.21	12	0.6 \pm 0.6
deciduous	569 \pm 42	10 \pm 1.0	9.5 \pm 1.2	15	0.07 \pm 0.03	0.07 \pm 0.02	13	0.9 \pm 0.9

^a Only one open automated wet deposition collector was deployed between 2001 and 2006; however, open area precipitation concentration data are presented here between 2001 and 2006 and also between 2005 and 2006 for direct comparison with Hg concentrations in throughfall and litterfall (Table 2) over these periods.

of snowpacks (L m⁻²) was determined from the weight of one snow core (1 g = 1 mL) collected using a 12.2-cm-diameter core tube. We compared average SWE data from these throughfall surveys with total SWE (from first snowfall until date of throughfall survey) measured using the meteorological site Nipher gauge. We then expressed throughfall snowpack SWE as a proportion of total open deposition. Using the average ratio of throughfall deposition to total open deposition for each throughfall site, we estimated throughfall snowpack SWE from the Nipher gauge for 2001–2006. During the open-water season in 1992–1999, open area wet deposition (millimeters of rain) was quantified using standard B-type rain gauges at the meteorological site. In the METAALICUS watershed from 2001–2006, standard B-type rain gauges positioned adjacent to the automated collectors were used to measure water deposition.

Annual THg and MeHg loadings were calculated for the water year (November 1–October 31) because snowfall following freeze-up in early November contributes to runoff the following spring. For each winter, net areal load of THg and MeHg in open area and throughfall snowpacks was calculated by multiplying the total areal water volume by the measured snowpack THg and MeHg concentrations for that year. If open area or throughfall snowpacks were not sampled for THg or MeHg concentrations in a given year, we used long-term average concentrations of these species in snowpacks from the surface of both Lake 239 and Lake 658 or near the specified automated throughfall collectors, respectively, for loading calculations.

During the open-water season, measured THg and MeHg concentrations were multiplied by areal water volumes of rain for individual sampling events and then summed to calculate a total loading for that year. For rain events that occurred before deployment of the collectors and after they were shut down in the fall, open loadings were estimated by multiplying areal water volume measured at the meteorological site by the average volume-weighted THg or MeHg concentration in rain for that year. For throughfall sites, open areal water volume for those missing periods was corrected by the average interception capacity of the canopy at that site before estimating the loading. For years when open area samples were not collected for Hg analysis (1993–1997), THg and MeHg loadings were estimated by using a long-term average concentration of each species in rain and the water deposition in the open for that year. SO₄²⁻ loadings associated with individual composite-sampling periods during the open-water season were similarly calculated.

For each litterfall collector, THg or MeHg concentrations were multiplied by corresponding litter mass loadings. Average annual litterfall THg and MeHg loadings at each site were calculated from the two replicate collectors.

Results and Discussion

Concentrations of THg and MeHg in Open Area Precipitation, Throughfall, and Litterfall. Concentrations of THg and MeHg in open area precipitation, throughfall, and litterfall are presented in Tables 1 and 2 and Figure S4 in the Supporting Information, whereas a more detailed discussion of the concentration data is presented in the Supporting Information. Concentrations of SO₄²⁻ in open precipitation and discussion of these data are also presented in the Supporting Information (Figure S5). However, caution is warranted when comparing concentrations of Hg in open precipitation with concentrations in throughfall because Hg concentrations in throughfall are higher not solely because of higher Hg deposition to foliage, but also because of water retention and evaporation in forest canopies. Hence, we focus here on comparing THg and MeHg loadings among our different sites and between geographical locations.

Annual THg and MeHg Loading Rates in Open Area Precipitation, Throughfall, and Litterfall. Annual open area loadings of THg and MeHg between 1992 and 2006 were 36 \pm 17 and 0.5 \pm 0.2 mg ha⁻¹, respectively (Figure 1). On average, 91 \pm 5 and 83 \pm 12% of annual open area loadings of THg and MeHg, respectively, occurred during the open-water season because of low water deposition during winter (average winter and open-water season millimeters of precipitation were 156 \pm 32 and 531 \pm 107, respectively), less efficient scrubbing of the atmosphere by snow than by rain 13, and photoreduction and emission of Hg in snow 12. Annual MeHg loadings in the open were not significantly related to THg loadings (p = 0.42, R^2 = 0.05). Annual average open area THg and MeHg loading rates are lower at the ELA than at all other sites in North America and Europe that have been previously studied (Table 3).

To directly compare loadings of THg and MeHg in the open with those in throughfall, we used only data collected at the METAALICUS watershed between 2001 and 2006 when our automated collectors in the open and under the forest canopy were operated simultaneously (Figure 2, Table S1 in the Supporting Information). Over this six-year period, the average annual THg loading in the open was 31 \pm 20 mg ha⁻¹ and there was no significant effect of time (year) on open area THg loading (two-factor ANOVA, p = 0.71) indicating

TABLE 2. Annual Mass Flux of Litter and Concentrations of THg and MeHg (\pm SD) in Litterfall under Four Forest Canopy Types at the ELA

site	annual litterfall mass flux (kg ha^{-1})	concentration (ng g^{-1})		<i>n</i>	% MeHg
		THg	MeHg		
2001–2006					
wetland	2824 \pm 1127	38.2 \pm 7.0	0.28 \pm 0.08	12	0.7 \pm 0.2
jack pine 1	3090 \pm 528	29.5 \pm 2.6	0.22 \pm 0.02	12	0.7 \pm 0.1
old growth 1	2365 \pm 527	48.4 \pm 9.6	0.37 \pm 0.05	12	0.8 \pm 0.2
2005–2006					
jack pine 2	3488 \pm 178	28.9 \pm 0.6	0.23 \pm 0.09	4	1.0 \pm 0.6
old growth 2	2000 \pm 313	69.2 \pm 10.0	0.29 \pm 0.12	4	0.7 \pm 0.2
deciduous	3188 \pm 248	29.3 \pm 0.9	0.49 \pm 0.14	4	0.8 \pm 0.4

no significant increase or decline in loading over that period. THg loadings were always higher under forest canopies than in the open (Figure 2). On average, at the two replicate old growth sites, throughfall THg loading ($123 \pm 41 \text{ mg ha}^{-1}$) was significantly higher than in the open (4.0 times, ANOVA, $p < 0.001$), under the jack pine forest ($51 \pm 17 \text{ mg ha}^{-1}$, 1.6 times open, $p < 0.01$), and under the deciduous forest ($p = 0.04$). THg loadings were consistently highest under old growth canopies than under all other forest canopy types, but no other statistically significant differences in THg loading rates were observed between forest types. The wetland ($83 \pm 26 \text{ mg ha}^{-1}$, 2.7 times open deposition) showed intermediate throughfall THg loading rates. Despite the deciduous canopy having the lowest THg loading rate of any of the forests studied ($45 \pm 0.5 \text{ mg ha}^{-1}$) and a relatively open canopy, there was still 1.5 times more THg deposited under this forest type than in the open.

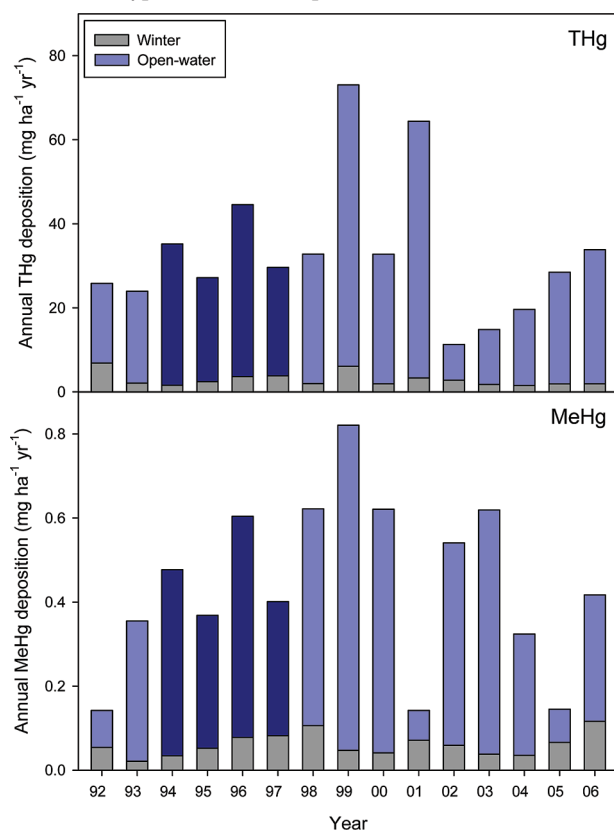


FIGURE 1. Annual winter and open-water season deposition of THg and MeHg in open area precipitation at the ELA. Dark blue bars represent years in which rain was not collected for THg and MeHg analysis. THg and MeHg loadings for these years are estimated using the long-term average concentrations of these Hg species in rain at the ELA.

Patterns of MeHg loadings under the different canopy types were less obvious than those observed for THg. There was no effect of time (year) on MeHg loading rates in throughfall (two-factor ANOVA, $p = 0.69$). On average, annual throughfall MeHg loadings followed the same general pattern as throughfall THg loadings, with the highest loading ($0.8 \pm 0.2 \text{ mg ha}^{-1}$) measured under the old growth canopy (2 times the open loading of $0.4 \pm 0.2 \text{ mg ha}^{-1}$). The next highest MeHg loadings occurred under the wetland canopy ($0.6 \pm 0.2 \text{ mg ha}^{-1}$, 1.3 times open loading) and jack pine canopy ($0.5 \pm 0.2 \text{ mg ha}^{-1}$, 1.1 times open loading). The only site with significantly greater MeHg loadings than in the open was the old growth site (ANOVA, $p = 0.045$), suggesting the possibility of in-canopy methylation and/or dry deposition of MeHg. If dry deposition of MeHg to forest canopies is occurring, it is certainly proportionately not as important in the boreal ecoregion as dry deposition of atmospheric Hg(II). Throughfall MeHg loadings under the old growth were also significantly higher than that under the jack pine canopy (ANOVA, $p = 0.043$); however, loadings beneath all the other canopies were not significantly different from each other or from MeHg loadings in the open. In fact, MeHg loadings under the deciduous canopy were on average lower than that in the open (0.4 ± 0.1 , 0.8 times open MeHg deposition), suggesting that there may be net retention or loss of MeHg within this forest type. The deciduous canopy in this study is very open, and there is the possibility that photoreduction and emission of wet-deposited MeHg as Hg(0) is higher here than in dense coniferous canopies.

Throughfall loadings of THg were almost as large as litterfall loadings in this study and much greater than deposition of THg in the open. The excess Hg(II) deposited beneath forest canopies in throughfall could be derived from several sources, but the primary source is thought to be washoff of previously dry-deposited HgP and RGM from foliage during precipitation events 23. However, it is difficult to reconcile these large throughfall loadings of THg with the extremely low concentrations of RGM measured at the ELA ($1\text{--}2 \text{ pg m}^{-3}$, unpublished data). Preliminary estimates of annual dry deposition of RGM to the region based on these concentrations, published deposition velocities, and leaf area index (LAI) were only $4\text{--}8 \text{ mg ha}^{-1}$, much lower than the $13\text{--}130 \text{ mg ha}^{-1}$ of net throughfall THg presented here. However, these previous estimates did not include measurements of atmospheric HgP. Another potential source of the Hg(II) in throughfall is direct oxidation of atmospheric Hg(0) to Hg(II) on the surface of wet foliage by ozone and subsequent washoff during precipitation events 20, 23. The final possible sources of the Hg(II) in throughfall are leaching and/or mechanical weathering of Hg from foliage itself. The Hg in foliage may have been derived via uptake of Hg(0) through open stomata or from root uptake, although the contribution from root uptake is thought to be minimal except in areas where soils are heavily contaminated with Hg 24.

TABLE 3. Loadings of THg and MeHg in Precipitation, Throughfall, and Litterfall at the ELA and at Other Sites

location	forest type	THg (mg ha ⁻¹)				MeHg (mg ha ⁻¹)				reference
		open	TF	LF	TF + LF	open	TF	LF	TF + LF	
North America										
ELA, Ontario, Canada; this study	old growth (jack pine, black spruce)	31	123	110	233	0.4	0.8	0.8	1.6	this study
ELA, Ontario, Canada; this study	wetland (black spruce, alder)	31	83	103	186	0.4	0.6	0.8	1.4	this study
ELA, Ontario, Canada; this study	deciduous (red maple, birch)	31	45	93	138	0.4	0.4	0.7	1.1	this study
ELA, Ontario, Canada; this study	jack pine	31	51	90	141	0.4	0.5	0.7	1.2	this study
ELA, Ontario, Canada; 1998/99	jack pine	70	80	120	200	0.9	0.9	0.8	1.7	10
Lake Champlain Basin, Vermont, USA	mixed hardwood	79	117	130	247					14
Walker Branch, Tennessee, USA	oak, hickory, pine	100	140	300	440					15
Lake Huron, Michigan, USA	mixed hardwood	49	67	114	181					16
Marcell Experimental Forest, Minnesota, USA	spruce peatland	65	130	123	253					17
Europe and Scandinavia										
Lehstenbach, Germany	Norway spruce	350	384	157	541	1.4	1.6	1.9	3.5	18
Steinkreuz, Germany	beech, oak	271	278	340	618	0.8	1.2	1.4	2.6	18
Lake Gårdsön, Sweden	hardwood forest	115	172	250	422	1.3	1.6	6.0	7.6	19, 20
Svartberget, Sweden	Norway spruce	70	150	180	330	0.8	1.7	3.0	4.7	21
Uraani, Finland	Norway spruce	51	158	372	530	0.9	1.4	2.7	4.1	22

Foliar washing experiments have shown that leaching is generally a less important process than washoff of Hg from leaf surfaces 25 and the contribution of mechanical leaf weathering to throughfall Hg fluxes is unknown (Supporting Information). Throughfall loadings of MeHg were also almost as large as litterfall loadings of MeHg in this study and higher than MeHg loadings in the open. A possible source of MeHg in throughfall is dry deposition of atmospheric MeHg 23. Additionally, chemical constituents that could fuel abiotic methylation (organic carbon compounds and abundance of

Hg(II)) are present in and on foliage. Subsequent washoff of MeHg produced abiotically within the forest canopy is therefore a possible source of the MeHg in throughfall 23, although we could not account for all the MeHg in throughfall by this process in our study (Supporting Information). Regardless of sources, throughfall THg and MeHg loading rates at the ELA are considerably and consistently lower than those at locations closer to more industrialized regions of North America and Europe (Table 3).

There is a great degree of interannual variation present in the loading rates of THg and MeHg both in the open and under the canopy in throughfall. Interannual variation in Hg loading at a given site is driven by interannual variations in both Hg concentration and water deposition. We used forward stepwise multiple regression to determine the relative importance of average concentration versus total water deposition to wet loading rates of THg and MeHg during the open water season for all sites. Average THg concentration explained 69.1% of the variation in THg loadings ($p < 0.001$). Adding water deposition to the regression explained an additional 19.5% of the variation ($p < 0.001$), for a total of 88.7% of the variation in THg loading explained by these two factors. For MeHg loadings, open season MeHg concentration was primarily responsible for driving variation in MeHg loadings (88.6% of variation explained, $p = 0.008$). The effect of water deposition was not significant for MeHg loading. The interannual variation in open and throughfall THg and MeHg deposition presented in this study shows the importance of long-term concentration data sets compared to short-term sampling regimes in understanding loadings of Hg to ecoregions.

Forests with greater LAI have higher foliar surface areas per unit ground area on which dry deposition of atmospheric Hg species can occur. LAI is defined as half the total leaf surface area per unit land surface area 26. We used triplicate hemispherical photographs to estimate average LAI for each throughfall site and examine the influence of LAI on patterns of Hg deposition in throughfall. Throughfall areal water loadings were inversely related to LAI (Figure S6 in the Supporting Information), whereas both THg and MeHg throughfall loadings were positively related to LAI (Figure 3). However, these relationships were not statistically significant. This lack of significance was primarily, but not entirely, driven

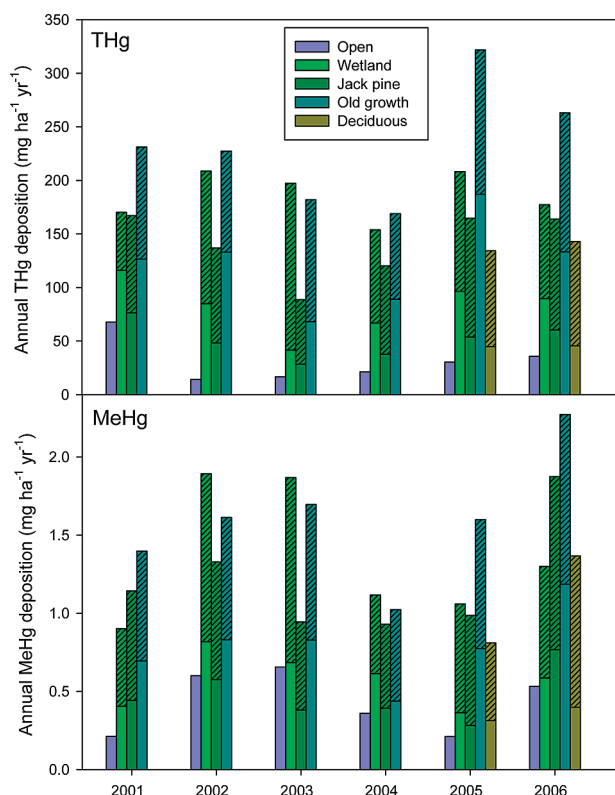


FIGURE 2. THg and MeHg deposition in open area precipitation, throughfall (stacked solid bars), and litterfall (stacked cross-hatched bars) under four different forest types at the ELA.

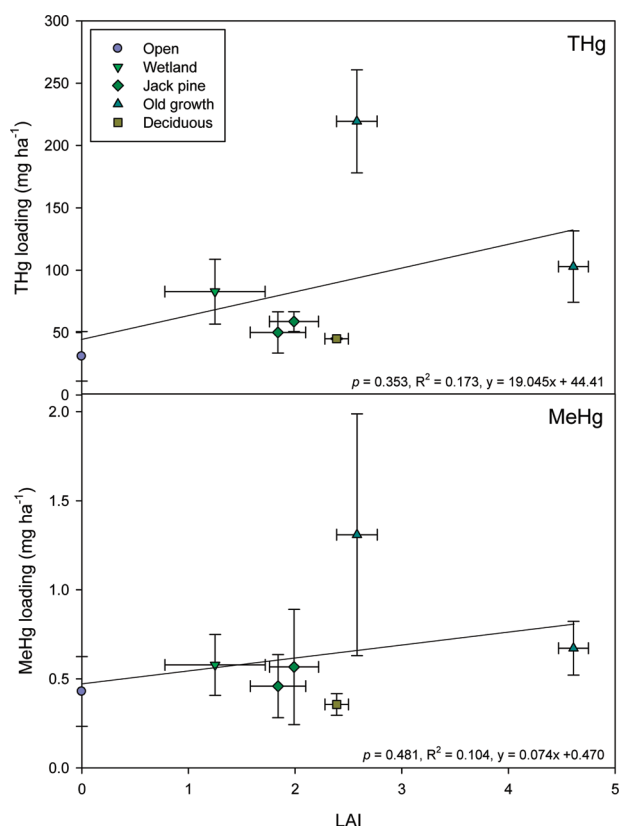


FIGURE 3. Relationship between LAI and annual THg and MeHg loadings in the open and under four different forest types at the ELA.

by the second old growth throughfall site added to our study in 2005. This site had 54.8% higher loadings of THg and 44.1% higher loadings of MeHg than the original old growth site. Even though the LAI at the second site was approximately half that at the original site, the average penetration of water through the forest canopy and the concentrations of THg and MeHg were 40, 55, and 44% higher than at the original site, respectively. The second site is located 44 m midway up a steep slope, whereas the original site is located in a sheltered area down near the lake, possibly resulting in less dry deposition of Hg and/or less water penetration during rain events. These differences in loading rates were observed within one 43-ha watershed and clearly illustrate the difficulties associated with trying to accurately quantify the dry deposition of Hg in a heterogeneous forest landscape and the importance of an adequate number of throughfall collectors to account for canopy heterogeneity.

The overall mean annual mass flux of litterfall at all our sites was $2800 \pm 400 \text{ kg ha}^{-1}$, $66 \pm 12\%$ of which occurred before the end of October. There was no significant difference between the annual mass flux of litterfall at the four different forest types (repeated measures ANOVA, $p = 0.224$), and there was no effect of time (year, $p = 0.18$) or any time \times forest type interaction ($p = 0.28$). Litterfall THg loading rates were not significantly different under the old growth ($110 \pm 21 \text{ mg ha}^{-1}$), wetland ($103 \pm 35 \text{ mg ha}^{-1}$), deciduous ($93 \pm 6 \text{ mg ha}^{-1}$), and jack pine canopies ($89 \pm 17 \text{ mg ha}^{-1}$, repeated measures ANOVA, $p = 0.35$). There was no significant effect of time (year) on litterfall THg loading rate ($p = 0.05$) or time \times forest type interaction ($p = 0.27$). MeHg loading rates were not significantly different under the old growth ($0.8 \pm 0.2 \text{ mg ha}^{-1}$), wetland ($0.8 \pm 0.4 \text{ mg ha}^{-1}$), deciduous ($0.7 \pm 0.2 \text{ mg ha}^{-1}$), and jack pine canopies ($0.7 \pm 0.1 \text{ mg ha}^{-1}$, repeated measures ANOVA, $p = 0.27$). There was no effect of time (year, $p = 0.114$), and no time by forest type interaction ($p = 0.480$).

Litterfall THg and MeHg loading rates at the ELA were generally consistent with other sites in North America, but lower than those from sites in Europe and Scandinavia that are more directly impacted by nearby industrial activity (Table 3). Hg(II) in litterfall is thought to be primarily derived from atmospheric Hg(0) taken up through leaf stomata that is oxidized to Hg(II) and retained until litterfall. However, the proportion of this Hg(0) that originates from ground emission below the canopy is unknown. Other smaller contributions could be provided by adsorption of previously wet- and dry-deposited Hg. As for throughfall, MeHg in litterfall could be derived from dry deposition of atmospheric MeHg or in-canopy methylation of Hg(II) 23.

While open areas receive most of their THg and MeHg loadings from rain (and a small contribution from direct dry deposition), loadings of THg and MeHg in both throughfall and litterfall must be added together to obtain net loadings of these species in forested areas (Table S1 in the Supporting Information). In this study, total net loadings of THg within forests ranged from 4 (for the deciduous forest) to 11 times (for the second old growth site) higher than in adjacent open areas. MeHg loadings followed a similar pattern ranging from 4 to 6 times higher (in these same forest types) than in the open, nearby. When monitoring net THg and MeHg deposition to watersheds, it is obviously not sufficient to measure open area loadings of these species alone. The strong amplifying effect of forest canopies on both THg and MeHg deposition must be considered and accounted for.

Revised Dry THg and MeHg Deposition Estimates for ELA Forests. Using the direct method of estimating dry deposition [(throughfall + litterfall) – open], we found that average annual estimates of dry THg deposition under the different forest canopies ranged from $105 \pm 2 \text{ mg ha}^{-1}$ (3 ± 1 times open THg loading) in the deciduous forest to $201 \pm 54 \text{ mg ha}^{-1}$ (8 ± 4 times open THg loading) at the old growth forest. Intermediate loadings were observed in the jack pine forest ($109 \pm 23 \text{ mg ha}^{-1}$, 5 ± 2 times open THg loading) and wetland ($155 \pm 35 \text{ mg ha}^{-1}$, 7 ± 5 times open). Average annual estimates of dry MeHg deposition showed the same general trend as THg loadings under the four different forest types and ranged from $0.7 \pm 0.2 \text{ mg ha}^{-1}$ (2 ± 1 times open MeHg loading) in the deciduous forest to $1.2 \pm 0.4 \text{ mg ha}^{-1}$ (3 ± 2 times open MeHg loading) at the old growth forest. MeHg loadings were intermediate in the jack pine forest ($0.8 \pm 0.4 \text{ mg ha}^{-1}$, 2 ± 2 times open MeHg loading) and wetland ($1.0 \pm 0.3 \text{ mg ha}^{-1}$, 2 ± 1 times open).

The difference between Hg loading in throughfall + litterfall and in the open is generally assumed to represent washoff of dry-deposited HgP and RGM and accrual of atmospheric Hg(0) by foliage 15, 20, 23. However, previously published results from the METAALICUS indicate that dry deposition is likely higher than these estimates because a portion of Hg from rain is returned to the atmosphere because of photoreduction to Hg(0) on foliar surfaces before washoff 27. In the recent METAALICUS synthesis, it was estimated that $\sim 25\text{--}30\%$ of the Hg(II) isotopes applied to the watershed was returned to the atmosphere via photoreduction (primarily from the forest canopy, with a smaller amount from ground vegetation; 2). If Hg(II) in rain behaves like the applied Hg(II) isotopes, then it is incorrect to assume that all Hg wet-deposited to the canopy is actually available to penetrate the canopy as throughfall. For example, when we remove that portion of Hg(II) that is photoreduced in the canopy itself (15–20%) and emitted back to the atmosphere, our annual dry deposition estimates increase by approximately 5–6 mg ha^{-1} , or 3–5% more (depending on the absolute magnitude of the dry deposition flux) than our previous estimates. While there is some preliminary evidence that MeHg deposited to foliage can also be photoreduced and/or retained (L. Mowat, unpublished data), there is currently not enough data to

estimate by how much MeHg dry deposition flux would increase if these pathways were accounted for.

In addition, it has been previously suggested that a portion of the Hg in rain binds to foliage and does not penetrate the canopy immediately as throughfall or may become irreversibly bound to foliage until litterfall. Dissolved Hg has a strong affinity for particulate matter, and any free Hg(II) in precipitation would be expected to bind quickly to foliar surfaces. In fact, at the end of three years of isotopic Hg(II) loadings to the METAALICUS watershed, on average $6 \pm 3\%$ of the applied watershed spikes were retained in the forest canopy. Since we are considering litterfall fluxes in this study, this fraction of wet-deposited Hg that becomes irreversibly bound to foliage is accounted for; however, in studies examining just net throughfall Hg inputs, the open deposition term should also be adjusted for this retention process or the dry deposition flux will be underestimated.

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Supporting Information Available

Details of analytical methodology and a discussion of the THg, MeHg, and SO_4^{2-} concentration data presented in this study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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